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On the dynamic roughening transition in nanocomposite film growth

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Surface roughness and dynamic growth behavior of TiC/a-C nanocomposite films deposited by nonreactive pulsed-dc (p-dc) magnetron sputtering were studied using atomic force microscopy, cross-sectional scanning, and transmission electron microscopy. From detailed analyses of surface morphology and growth conditions, it is concluded that a transition in growth mechanisms occurs, i.e., a mechanism dominated by geometric shadowing at a p-dc frequency of 100 kHz evolving to a surface diffusion mechanism driven by impact-induced atomistic downhill flow process by Ar^+ ions at a p-dc frequency of 350 kHz. It is shown that rapid smoothening of initially rough surfaces with rms roughness from $\sim$6 to $<$1 nm can be effectively achieved with p-dc sputtering at 350 kHz pulse frequency, leading to a transition from a strong columnar to a columnar-free microstructure. © *2009 American Institute of Physics*. [doi:10.1063/1.3262952]

Surface smoothness of thin films based on diamondlike carbon (DLC) becomes a crucial property for developing nearly frictionless protective coatings. In the case of rough sliding surfaces, a high level of mechanical interlocking between surface asperities leads to high friction and wear (especially during the run-in period). A rough surface of films may result from the type of deposition process used and also from the initial roughness of substrate. For industrial applications, one of the major concerns is to obtain smooth films on rough substrates, i.e., how rough the finishing of substrates can be smoothened in film deposition.

Pulsed-dc (p-dc) magnetron sputtering is one of the powerful and versatile techniques to produce DLC based films.[1] During sputtering deposition, there is an interplay among interface roughening generated by random deposition of atoms, smoothening driven by surface diffusion due to concurrent ion impingement and nonlocal effects generated by shadowing. Geometrical shadowing, which is the result of deposition by non-normal incident flux,[2] enhances growth front roughness. Without additional lateral relaxation processes, this would inevitably cause dynamic roughening, i.e., increase of surface roughness as a function of deposition time.[3] The growth mechanisms essentially govern the microstructure and thus influence the mechanical and tribological properties of these films. Over the past decade considerable attention has been paid to the theoretical and experimental aspects of dynamic roughening of films grown on smooth surface,[4–7] whereas little attention has been paid to films grown on rough surfaces where smoothening phenomenon may occur.[8–10] Recently, we have reported that dynamic growth behavior of thick TiC/a-C films grown by p-dc sputtering on smooth surface depends upon the applied pulse frequency.[11] At higher pulse frequency, dynamic roughening was completely suppressed and rather dynamic smoothening was revealed.[12] However, the question remains: Can dynamic smoothening be achieved for these films grown on initially rough surfaces?

In this letter, we utilize the fact that pulse frequency has prominent effect on the energy distribution and flux of impinging ions on a growing film[13] to investigate the evolution of surface morphology during p-dc magnetron sputtering. Dynamic roughening of TiC/a-C films grown on smooth surface at low pulse frequency (100 kHz) on purpose to simulate a rough finishing of industrial substrates and then rapid smoothening of such initial rough films at higher pulse frequency (350 kHz) has been reported.

TiC/a-C nanocomposite films were grown on Si wafer using close field unbalanced magnetron p-dc nonreactive sputtering deposition. The detailed setup has been described elsewhere.[13] It consists of four magnetrons coupled to one Ti and one Cr target powered by dc power supply and two graphite targets opposite to each other powered by pulsed-dc power supply, respectively. All the power units for sputtering worked at current-control mode. The substrates, located at 80 mm distant from the targets, were biased by p-dc at -40 V and 250 kHz frequency. No intentional heating was applied to the substrates. To study the dynamic growth behavior, series of TiC/a-C top layers were deposited for various deposition times and at two p-dc frequencies, coded as xxx-CyyyTi where xxx denotes p-dc frequency powering the graphite (C) targets in kilohertz and yyy the sputtering current applied to Ti-target in ampere. The p-dc current applied to the graphite targets was always 1.5A each. The deposition rates were 8.0, 8.5, and 3.15 nm/min for 100C0.35Ti, 100C0.55Ti, and 350C0.35Ti, respectively.

Figure 1 presents the surface roughness evolution of TiC/a-C films as a function of deposition time and frequency of p-dc sputtering graphite targets. It is interesting to note that the surface roughness of the layers deposited at 100 kHz p-dc frequency experiences continuous roughening and those of 350 kHz p-dc sputtered layers exhibit dynamic smoothening instead. In addition, the sputtering current applied to Ti-target also plays a role. By intentional use of different currents to Ti-target, two different levels of roughness have been

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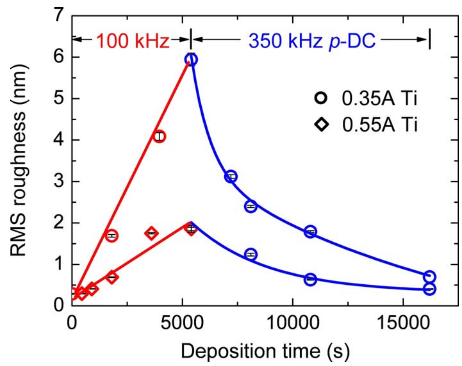

FIG. 1. (Color online) Surface rms roughness of TiC/a-C films as a function of deposition time and p-dc frequency. Rapid smoothening effect was fitted by exponential decay for the 350C0.35Ti top layers.

achieved after 90 min deposition with 100 kHz p-dc sputtering, i.e., 5.93 ± 0.15 nm with 0.35 A and 1.85 ± 0.04 nm with 0.55 A current to Ti target, respectively. Thereafter, rapid smoothening has been observed with 350 kHz p-dc sputtering, i.e., no matter how high the initial roughness was. Within a limited deposition time of 180 min, however, the final roughness is related to the initial roughness.

The change in pulse frequency causes a transition of dominating growth mechanism that controls the film growth. To understand the growth mechanism the films were further investigated with height-difference correlation function $\mathrm{H}(r)=\langle[\mathrm{h}(\mathrm{x})-\mathrm{h}(\mathrm{x}+r)]^2\rangle$, where h(x) is the height at a position x on the surface. The notation $\langle\cdots\rangle$ denotes the statistical ensemble average along the fast scan direction for all the points apart by a distance of r. The height-difference correlation function takes the form $\mathrm{H}(r)\sim r^{2\alpha}$ for $r \ll \xi$ and $\mathrm{H}(r) \sim 2w^2$ for $r \gg \xi$, where ξ is the lateral correlation length, w is the interface width or rms roughness, and α is the roughness exponent. In the dynamic scaling hypothesis for self-affine film growth, both w and ξ grow as a power law with time: $w \sim \mathrm{t}^{\beta}$ and $\xi \sim \mathrm{t}^{1/z}$, where the exponents β and z are called the growth exponent and dynamic exponent, respectively. Dynamic scaling requires $z=\alpha/\beta$.[3] The values of α and ξ for 100C0.35Ti series have been calculated from the height-difference correlation function, and the exponent 1/z have been calculated from the log-log plot of ξ versus growth time. Consecutively, β has been calculated, by using $z=\alpha/\beta$, as 0.53 ± 0.02. Alternatively, β has been calculated from the log-log plot of w versus growth time as 1.13. The considerable difference in the values of β implies the breakdown of self-affinity of the system due to presence of nonlocal growth effects such as geometrical shadowing.[14] This is well supported by previous theoretical or experimental studies which revealed that if the geometrical shadowing effect dominates in the film growth the value of β will be equal to or above 0.5.[15–18] Similarly for 100C0.55Ti films, the scaling relationships between the exponents cease to exist, the power law scaling behavior gives $\beta=0.84$. Thus, increasing the current of Ti target to 0.55A reduces the absolute value of the interface width as well as the value of β, indicating that the interface width grows less rapid than that of the 100C0.35Ti films. This is due to increased Ar^+ ion flux impinging at the growing interface with increasing target current. Thus geometrical shadowing, where taller surface features block the nonnormal incident flux from reaching lower-lying areas of the surface, dominates the film growth to yield dynamic roughening in 100 kHz p-dc sputtered films.

The dramatic decrease in the surface roughness as a function of growth time during 350 kHz p-dc sputtering is interesting since it indicates the presence of surface diffusion driven growth. The log-log plot of w versus growth time for 350C0.35Ti films gives values of β as -0.76 and -0.96, respectively, indicating surface smoothening. The flux and energy distribution of impinging ions (primarily Ar ions[13]) at the growing interface play a crucial role in achieving the smoothening effect.[12] During 350 kHz p-dc sputtering a high Ar^+ ions and energy flux was delivered to the growing film.[13] Also the plasma fills in the whole chamber ensuring continuous impingement of the growing film in a closed-field unbalanced configuration.[13] The intensive ion impingement on the growing interface provides an important contribution to the surface diffusion of adatoms during the film growth. Furthermore, the Ar^+ ions impinge more likely at the surface protrusions or hills rather than in the valleys. It means that the ion impingement can erode hills and fill in the valleys. At the final stage of the growth at 180 min, the surface becomes smoother and the peak-to-valley distance becomes smaller. The value of α, calculated from height-height correlation function, for these films show decreasing trend from 0.7 to 0.5 with increasing growth time indicating formation of subnanometer crater formation in the vicinity of impact site. This contradicts with the smoothening due to local melting induced by thermal spikes proposed by Casiraghi *et al.*[19] It is believed that the intensive and continuous impingement with high flux and high energy ions causes impact induced downhill flow of adatoms in the presence of top amorphous layer[11] as proposed by Moseler *et al.*[20] This surface diffusion competes with the geometrical shadowing and noise induced roughening to evolve surface smoothening. However, during 100 kHz p-dc sputtering, the Ar^+ ion and energy flux is quite low compared to the case of 350 kHz p-dc sputtering. Also the plasma does not cover the whole chamber.[13] Under these growth conditions the surface diffusion does not provide enough lateral relaxation yielding dynamic roughening. Another contribution to the increase in roughness may be the strength of the shot noise, which is expected to increase with deposition rate.[21]

Figure 2 shows the microstructural evolution of the films 100C0.35Ti-350C0.35Ti and 100C0.55Ti-350C0.35Ti, respectively. During 100 kHz p-dc sputtering, the microstructure shows strong columns but evolves as dense and noncolumnar structure in the onset of 350 kHz p-dc sputtering. Nevertheless, a smaller surface roughness corresponds to a weaker character of columnar microstructure in the 100C0.55Ti layer [see Figs. 1 and 2(b)]. cross-sectional transmission electron microscopy (XTEM) was also performed to reveal the internal structure evolution during growth of the film along the thickness direction. As shown in Fig. 3, both the 100 kHz layer and the 350 kHz layer exhibit multilayered structures, due to the phase separation occurred during deposition (details out of the scope of this letter). The column boundaries grown during 100 kHz p-dc sputtering are indicated by open triangles in Fig. 3. In the early period of 100 kHz p-dc deposition, the columns do not develop due to a low surface roughness. Rather, the columns gradually occur and rapidly grow when the film grows to a thickness of approximately 200 nm, as shown by both the cross-sectional scanning electron microscopy (XSEM) and XTEM micro-

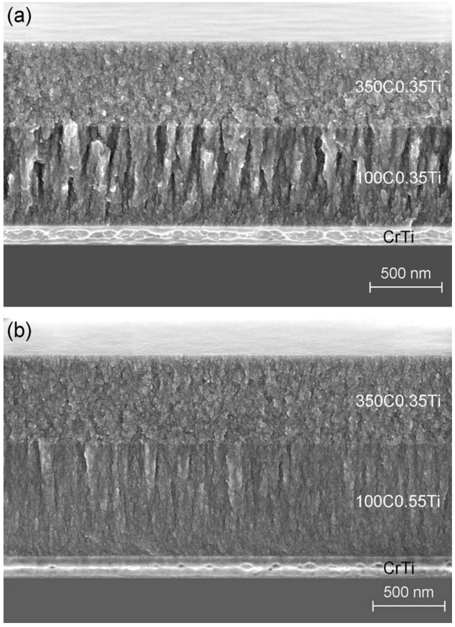

FIG. 2. Cross sectional SEM of TiC/a-C films deposited with p-dc sputtering graphite targets first at 100 kHz for 90 min and then at 350 kHz for 180 min: (a) 100C0.35Ti-350C0.35Ti and (b) 100C0.55Ti-350C0.35Ti. Immediate transition of microstructure from columnar to column-free is observed at the switch of p-dc sputtering frequency.

graphs in Figs. 2 and 3. Considering the roughness evolution with time for 100C0.35Ti films (Fig. 1), it is evident that the rapid growth of columns is directly in accordance with the steep increase in surface rms roughness from approximately 1.6 nm at 30 min to 4 nm at 60 min. It is important to note that increasing the current to Ti target gives a weak columnar structure as shown in Fig. 2(b) compared to Fig. 2(a) during 100 kHz p-dc sputtering. The immediate suppression of the columnar structure was apparent and independent of surface roughness in both the cases of 350 kHz p-dc deposition, and the structure evolves as fully homogeneous within 100 nm thickness growth. Correspondingly, the roughness developed during 100 kHz deposition was smoothed out rapidly by the following 350 kHz deposition as clearly revealed by the XTEM observation.

As the chemical structure (sp^2/sp^3 content) of the film depends upon the ion energy delivered to the film, sp^3 (diamond like phase) content in the film in the regime p-dc 350 kHz is believed to be more than at p-dc 100 kHz. High energy high flux impinging ions at p-dc 350 kHz lead to a high internal stress ($\sim$3 GPa compressive; measured by Si wafer curvature measurement) which favors formation of a dense diamond like phase. Thus the ion energy appropriate for diamond like film formation may be associated with a smooth surface while that for graphitic film formation may be associated with rough surface.[22]

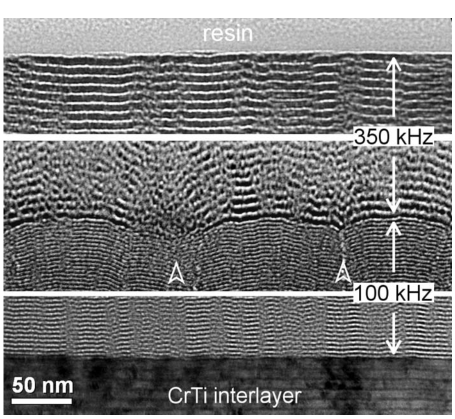

FIG. 3. Cross-sectional TEM micrograph of the TiC/a-C film 100C0.55Ti-350C0.35Ti. The evolution of the multilayered structure clearly reveals that the increased roughness during 100 kHz p-dc sputtering was smoothened out by the following 350 kHz p-dc sputtering.

In conclusion, we have studied the dynamic growth behavior and the corresponding microstructural evolution of p-dc sputter-deposited TiC/a-C nanocomposite films at two pulse frequencies. It is shown that surface smoothening of initially rough surface ($\sim$6 nm RMS roughness) can be effectively achieved during 350 kHz p-dc sputtering. Our analyses show that observed decrease in surface roughness and the microstructure evolution are the result of intensive concurrent ion impingement at 350 kHz frequency, which provides the lateral surface relaxation and suppresses the geometrical shadowing effect. The observed dynamic smoothening phenomenon is not restricted to the TiC/a-C nanocomposite films. It can also be applied to other amorphous coatings deposited with high ion energy.

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